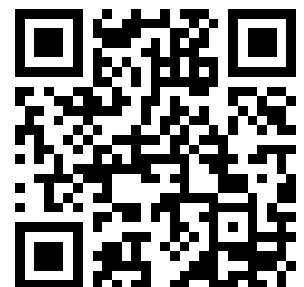

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STUDIES ON THE POLYMORPHS OF HMX



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STUDIES ON THE POLYMORPHS OF HMX

Work done by:

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ABSTRACT

The sensitivities of the HMX polymorphs have been studied in the Type 12 impact machine, with and without sandpaper. The order of sensitivities may be summarized as $\delta > \gamma > \alpha > \beta$. However, a wide range of 50% points was obtained with the various samples of α - and γ -HMX which were tested. The sensitivity of γ -HMX depends on the particle size, the larger particles being more sensitive. No explanation was found for the variability in the sensitivity of α -HMX.

Both α - and γ -HMX form readily under conditions likely to be encountered in the processing of explosives. α -HMX forms at an evaporating solvent-container interface, whether β -HMX is present or not. γ -HMX is formed during steam distillation of HMX solutions in various solvents, and on precipitation of HMX from water-miscible solvents by dilution with water. However, in the presence of a solvent the conversion of γ to β is rapid providing crystals of β are present initially.

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I. INTRODUCTION

HMX is an explosive of considerable interest in itself and also because it is present in significant amounts (commonly around 6%) as an impurity in Bachmann-process RDX. It is unusual among high explosives as it has four readily-formed and well-recognized polymorphs. β -HMX is the stable form and is the polymorph usually referred to when the unqualified name HMX is used. Its properties as an explosive closely resemble those of RDX, and its presence in RDX is not usually considered to be a cause for concern. On the other hand, the other three polymorphs have all, at one time or another, been alleged to be dangerously sensitive materials, and their unexpected appearance in β -HMX or in RDX could, therefore, lead to serious accidents. It is these considerations which have led a number of investigators to study the properties of the polymorphs of HMX. Unfortunately, the results of the various investigations are not in satisfactory agreement as to the ease of formation and the sensitivities of the unstable forms. The work reported here was undertaken at Los Alamos several years ago in the hope that we could resolve these difficulties and has been in progress, off and on, to the present time. Some of the contradictions from earlier work have been resolved, and some experimental observations of practical importance have been made. However, it is evident that we still have not achieved a satisfactory understanding of the HMX system, particularly with respect to the difficult but all-important sensitivity problem.

II. HMX SOURCES

The starting material used in most of our work was a specially purified HMX obtained from Holston. This material was identified as Lot No. SR-164-58, Ba 447. The specifications to which it was made require that the RDX content in the final product be less than 0.5%. It was made by percolating acetone through regular production HMX until the RDX crystals were dissolved out. The HMX itself was not recrystallized in this process. Our analysis of this material indicated that the HMX was entirely in the form of the β polymorph, that it contained something less than 0.5% formaldehyde polymers, and that the final RDX content was about 0.1%. The RDX was probably present as a solid solution in the HMX, as no distinct crystals of RDX could be detected by microscopic, infrared, or X-ray methods. This material will be referred to as "99.5% β -HMX" in the subsequent sections of this report.

Other samples of U. S. manufacture used in this work were obtained from standard Holston production lots. They are identified by lot numbers as follows: 554-54, 41-57 (4.85% RDX), and 166-54 (3.40% RDX).

Some work also was done with a sample of HMX received from the British. This sample contains less than 0.1% RDX and will be referred to as UK β -HMX in this report.

III. PREPARATION OF THE PURE POLYMORPHS

A. β -HMX

Other than direct use of β -HMX as received, it was possible to obtain β -HMX by recrystallization of HMX from any solvent at temperatures below 102°C by appropriate conditions of stirring and time. β -HMX referred to as "recrystallized β -HMX" was prepared by saturating acetone with 99.5% β -HMX, adding water to precipitate γ -HMX, and stirring until the γ -HMX was reconverted to β -HMX. The crystal size of the recrystallized β -HMX was controlled by the stirring rate and the acetone-water ratio.

B. α -HMX

The methods used for the preparation of α -HMX were modifications of methods described in earlier reports on the HMX polymorphs^{1, 2}. These modifications were necessitated by effects caused by the low atmospheric pressure at Los Alamos. Lowered boiling points and decreases in HMX solubility in a solvent at its boiling point were the principal effects which had to be considered.

One method used for the preparation of α -HMX was to cool slowly a hot concentrated solution of HMX in 70% nitric acid, as described by Blomquist¹. A second method was to reflux a slurry of HMX with acetic acid, propionic acid, or a mixture of the two acids as described in an Armour Research Foundation report³. Other methods used for small scale preps were recrystallization from 25% nitric acid, 50% acetic acid, or CEF [tris(β -chloroethyl)phosphate] at 157°C. Massive α -HMX

was most easily prepared using conditions under which α -HMX was the stable polymorph.

C. γ -HMX

Three methods were used to prepare one to five gram quantities of γ -HMX. Small to medium sized crystals of γ -HMX were prepared by mixing a solution of HMX in acetone with water. The maximum dimensions of the largest plates formed could be varied between 1 and 60 μ depending upon the rate of dilution of the acetone solution. Medium sized crystals, with the maximum dimension of the largest crystals between 50 and 200 μ , were prepared by stripping the solvent from a cyclohexanone solution of HMX by sparging with steam. Myers and Bedard³ first described this preparation method. The third method was used to prepare crystals over 400 μ in the maximum dimension. The procedure was to dissolve 2 gm of HMX in 50 cc of boiling 70% nitric acid in a 125 ml flask, cool rapidly under a stream of cold water while swirling, and after crystallization filter, wash with water, and dry.

Several other methods for preparing γ -HMX, described as producing massive γ -HMX, were tried in hopes of obtaining untwinned crystals for study. None of these methods were successful. A method was developed which gives a satisfactory yield of single untwinned massive γ -HMX crystals. This preparation gives a mixture of γ - and β -HMX. About 25 cc of a solution of HMX in acetone was evaporated rapidly, without boiling, from a petri dish. The evaporating solution was

seeded continuously with γ -HMX by adding water dropwise. Soon after it was obvious that the seed crystals were growing rapidly, the remaining solvent was decanted and the crystals were dried. Good crystals up to 200 μ on a side were formed in this way.

D. δ -HMX

One to three gram quantities of δ -HMX were prepared in two ways. The simplest was to heat 99.5% β -HMX at temperatures between 159°C and 165°C, or over 190°C. The higher the temperature the shorter the time required for conversion. The size of the δ -HMX crystals could be controlled by the size of the β -HMX crystals since the β -HMX crystals usually transformed into single δ -HMX crystals if the temperature was below 162°C. β -HMX free of RDX was not satisfactory for this preparation. See the discussion on solid-solid transformations for details.

The other large scale preparation method for δ -HMX was recrystallization from a slurry of β -HMX in CEF at 160°C. It was necessary to use β -HMX which had been purified with respect to RDX to prevent solid-solid transformation. The final slurry of δ -HMX in CEF was filtered hot, and the remaining solvent was removed by washing the crystals with a dilute solution of acetone in toluene. Massive crystals of δ -HMX over 1 mm in diameter could be formed in this way.

Fine crystals of δ -HMX were prepared by heating 99.5% β -HMX at temperatures over 190°C or by rapid recrystallization from acetic acid as described by Blomquist¹.

IV. PROPERTIES OF THE POLYMORPHS

Only properties which have been studied here will be discussed.

A. Melting Point of HMX

The melting point of some specially purified HMX was determined by standard capillary and hot bar techniques. The measured melting point is time dependent, indicating that decomposition products are lowering the melting point. Heating at 1°C/min from room temperature gives a mp of 262°C by the capillary method. The first time the melting point was run in this manner, the HMX in the 0.8 mm capillary exploded at about 262°C. All later runs gave melting with decomposition. Faster heating rates give higher melting points, and the hot bar indicates a melting point of 279°C. Literature values of 278°-280°C^{11,12,13} agree with the latter figure.

B. Temperature Stability Ranges of the Polymorphs

The literature on the temperature ranges in which the different HMX polymorphs are stable is contradictory. The reported stability ranges and our results are summarized in Table I.

The transition temperatures were checked using CEF as a solvent on the hot stage of a microscope. The criterion for stability of polymorph "b" with respect to polymorph "a" was that "a" be transforming to "b" at a detectable rate at the given temperature. Transitions in both directions were checked, i.e., "b" to "a" and "a" to "b". Where a range of temperatures is given, the transformation rates were too slow to be observed. The pressure on the system was 580 mm instead

Table I

Temperature Stability Ranges of the Polymorphs

	<u>β-HMX ($^{\circ}$C)</u>	<u>α-HMX ($^{\circ}$C)</u>	<u>γ-HMX ($^{\circ}$C)</u>	<u>δ-HMX ($^{\circ}$C)</u>	<u>Ref.</u>
13	R.T. to 146-150	146-150 up to 156-158.5	metastable	156-158.5 to mp	1
	" " 115	115 " " 156	156°	156 " "	4
	" " 105	105 " " 155	metastable	155 " "	14
	" " 102-104.5	102-104.5" " 160-164	"	160-164 " "	This work

of 760 mm; however, this should not appreciably affect the results. The results indicate that the β - α transition temperature is between 102 and 104.5°C, the β - δ transition temperature is between 149 and 151°C, and the α - δ transition temperature is between 160 and 164°C. γ -HMX was metastable at all temperatures checked, and, in particular, γ -HMX was highly unstable with respect to both α - and δ -HMX between 150 and 160°C.

The behavior of all the polymorphs in the presence of solvents is in agreement with the measured stability ranges. α -HMX often appears to be stable under anomalous conditions. These conditions are discussed in a later section of this report.

C. Impact Sensitivity Data

1. Sensitivities of the Polymorphs

The impact sensitivities of the HMX polymorphs have been studied by Blomquist¹; Bachmann, Blomquist, Davy, MacDougall, and Whitmore¹⁷; Rosen, Taylor, and Wintermeyer¹⁸; Myers and Bedard³; Jeffers¹⁸; and Batty and Gilbert¹¹. The investigations reported in refs. 1, 17, and 18 (especially the last) are the most comprehensive. Jeffers' work was done on the Rotter impact machine while our work, which parallels much of his, was done on the ERL Type 12 and 12B designs. The usual 50% points obtained for PETN, RDX, and HMX on the ERL machines are as follows:

	<u>50% Point (cm)</u>	
	<u>Type 12</u>	<u>Type 12B</u>
PETN	12	30
RDX	22	47
HMX	26	32

The Type 12B and Rotter machines both indicate that RDX is less sensitive than HMX. In the Type 12 device, RDX is invariably found to be slightly more sensitive than HMX. Results obtained in the Type 12 machine exhibit a high degree of reproducibility, while considerable day-to-day scatter is observed in the Type 12B device.

A summary of the data obtained on the HMX polymorphs is given in Tables II, III, IV, and V. The preparative methods referred to in the tables are as follows:

<u>Number</u>	<u>Method</u>
1	Recrystallization from acetone by dilution with water
2	Azeotropic distillation of cyclohexanone from HMX solution
3	Recrystallization from 70% nitric acid
4	Reflux HMX slurry in mixture of acetic and propionic acids
5	Reflux HMX slurry in propionic acid
6	Reflux HMX slurry in acetic acid
7	Heat recrystallized β -HMX at 175°C
8	Recrystallize from aqueous acetone
9	Recrystallized from CEF at 159°C
10	Heat 99.5% β -HMX at 160-165°C
11	Heat 99.5% β -HMX at 190°C
12	Heat U K HMX at 190°C for 15 hours

We had hoped that a reasonably clear picture of the sensitivities of the HMX polymorphs, and of the factors influencing these sensitivities, would result from these studies; however, a glance at the tables will indicate that this expectation was not realized, and we are reduced to drawing some rather general conclusions about the behavior of these materials. Reference to Fig. 1, where the data are summarized graphically, may be of some assistance in this connection.

We first of all note that reasonably reproducible results were obtained only on the β and δ polymorphs. The samples of δ tested were,

Table II - β -HMX

Sample Composition (wt percent)	Average diameter of Crystals (μ)	Preparation Method	Test Sample		Standard HMX (99.5% β -HMX)			
			$\frac{h(\text{cm})}{m(\log)}$	$\sigma(\log)$	$\frac{h(\text{cm})}{m(\log)}$	$\sigma(\log)$		
T 100 β	21	1	21.2	1.3259	0.049	26.7	1.4259	0.036
Y 100 β	75	2	24.2	1.3843	0.036	24.5	1.3885	0.026
P 100 β	140	1	24.9	1.3968	0.047	26.7	1.4259	0.036
E 100 β	350	UK HMX	23.7	1.3759	0.049	24.0	1.3801	0.050
T 100 β	350	UK HMX	44.2	1.6453	0.104	34.2	1.5341	0.089
Y 100 β	350	UK HMX	33.1	1.5201	0.061	28.2	1.4501	0.055
P 100 β	350	UK HMX	29.9	1.4760	0.049	33.3	1.5218	0.054
E 100 β								
12B								

NOTE: The Type 12-B data were obtained in three tests made at different times with the same standard and test samples of HMX. These results illustrate the irreproducibility of the Type 12-B device.

Table III - α -HMX

	Sample Composition (wt percent)	Prep ¹ Meth	Crystal Thickness			Residual solvent (wt percent)	Test Sample			Standard HMX (99.5% β HMX)	
			larger unstriated α -HMX (μ)	larger striated α -HMX (μ)	γ -HMX (μ)		h(cm)	m(log)	σ (log)	h(cm)	m(log) σ (log)
T Y P E 12	100 α	3	15 μ	100 μ			15.6	1.1926	0.031	25.7	1.4093 0.022
	100 α	4	35	100			19.7	1.2938	0.063	27.7	1.4426 0.045
	100 α	4	40	120			19.7	1.2938	0.063	27.7	1.4426 0.045
	95 α , 5 γ	3	7	20	10		20.6	1.3134	0.061	25.7	1.4093 0.022
	100 α	3	20	80			21.2	1.3259	0.049	25.7	1.4093 0.022
	99 α , 1 γ	3	7	12	10		21.6	1.3343	0.036	26.2	1.4176 0.018
	100 α	5	20	60		0.5	22.2	1.3468	0.034	25.7	1.4093 0.022
	99 α , 1 β	6	12	25			22.9	1.3593	0.063	26.2	1.4176 0.018
	75 α , 25 β	7	3	3			23.2	1.3651	0.036	26.7	1.4259 0.036
	100 α	4		300			25.7	1.4093	0.022	24.9	1.3968 0.034
	100 α	5	30	40		0.7	26.4	1.4210	0.018	25.7	1.4093 0.022
T Y P E 12B	90 α , 9 β , 1 γ	3	10	12	30	0.5	15.0	1.1759	0.049	26.7	1.4260 0.049
	98 α , 2 β	3 ^a	40	210		0.31	15.3	1.1843	0.063	39.2	1.5926 0.045
	98 α , 2 β	3 ^a	40	210		0.13	18.5	1.2676	0.045	39.2	1.5926 0.045
	100 α	4	40	120			19.2	1.2843	0.090	26.7	1.4259 0.049
	100 α	4	20	200			25.2	1.4009	0.036	26.7	1.4259 0.049
	100 α	4	10	100			25.3	1.4038	0.054	26.7	1.4259 0.049
	100 α	4	35	100			25.4	1.4051	0.023	26.7	1.4259 0.049
	100 α	3	15	50		0.28	26.2	1.4176	0.072	33.6	1.5260 0.049
	100 α	3	25	40		0.13	26.9	1.4301	0.043	33.6	1.5260 0.049
	100 α	3	15	100			30.2	1.4801	0.097	26.7	1.4259 0.049
	100 α	3	40	70		0.36	30.8	1.4885	0.054	33.6	1.5260 0.049
	100 α , trace γ	3	50	225	20	0.40	37.3	1.5718	0.041	33.6	1.5260 0.049
	100 α	4	30	40		0.7	41.1	1.6134	0.034	26.7	1.4259 0.049
	98 α , 2 γ	3	15	140	5	0.39	41.9	1.6218	0.054	33.6	1.5260 0.049
	100 α	6	18	60			43.6	1.6392	0.073	37.7	1.5760 0.023
	100 α , tr β , γ	3	10	100	--		48.4	1.6843	0.049	26.7	1.4259 0.049
	90 α , 10 γ	3	10	80	20	0.8	50.7	1.7051	0.055	26.7	1.4259 0.049
	99 α , 1 γ , tr β	3	10	40	10		56.6	1.7529	0.050	37.7	1.5760 0.049

¹ Refer to text² + vacuum dry

Table IV - γ -HMX

	Sample Composition (wt percent)	Prep Meth	Crystal Size			Test Sample			Standard HMX (99.5 % β -HMX)		
			Thickness of larger(μ)	Ave dia (μ)	Max dim larger(μ)	h(cm)	m(log)	σ (log)	h(cm)	m(log)	σ (log)
T Y P E 12	100 γ	2	20	20	100	13.8	1.1385	0.068	25.9	1.4134	0.021
	100 γ	2	15	20	90	13.9	1.1426	0.031	24.5	1.3885	0.026
	100- γ , trace β	1	15	15	50	14.6	1.1634	0.141	25.9	1.4134	0.021
	100- γ , trace α	3	100	80	400	16.2	1.2093	0.063	25.9	1.4134	0.021
	98 γ , 2 β	1	9	13	30	18.2	1.2593	0.053	26.2	1.4176	0.030
	99.5 γ , 0.5 α	2	10	20	100	18.7	1.2710	0.029	24.5	1.3885	0.026
	80 γ , 20 α	3	25	60	350	18.9	1.2759	0.054	25.7	1.4093	0.022
	99.9 γ , 0.1 α	2	10	30	120	19.8	1.2968	0.017	24.5	1.3885	0.026
	80 γ , 20 β	1	15	10	100	20.1	1.3028	0.049	26.2	1.4176	0.030
	95 γ , 5 β	1	10	12.5	40	20.4	1.3093	0.049	26.2	1.4176	0.030
	99 γ , 1 β	8	25	35	130	20.4	1.3093	0.020	24.5	1.3885	0.026
	100 γ	1	4	8	20	21.8	1.3392	0.073	25.9	1.4134	0.021
T Y P E 12B	100 γ	1	<1	2	8	23.1	1.3634	0.088	25.9	1.4134	0.021
	100 γ	1	1	3	10	26.9	1.4301	0.056	26.2	1.4176	0.030
	100 γ	1	<1	<1	4	28.5	1.4551	0.077	25.4	1.4051	0.013
	100 γ	1	2	7.5	16	29.6	1.4718	0.068	26.2	1.4176	0.030
	100 γ	1	<1	1	8	31.1	1.4926	0.018	26.2	1.4176	0.030
	100 γ	1	1	2	8	33.9	1.5301	0.029	25.4	1.4051	0.013
	100- γ , trace α	3	100	80	400	12.4	1.0937	0.072	36.6	1.5634	0.047
	80 γ , 20 α	3	25	60	350	15.4	1.1884	0.090	26.7	1.4259	0.049
	100 γ	2	20	20	100	15.7	1.1968	0.047	33.3	1.5218	0.041
	100- γ , trace β	1	15	15	50	17.2	1.2343	0.049	33.3	1.5218	0.041
	100- γ , trace α	2	8	15	60	23.0	1.3619	0.036	35.2	1.5468	0.047
	99 γ , 1 α	8	25	35	130	23.5	1.3718	0.041	35.2	1.5468	0.047
	100 γ	1	<1	2	8	34.2	1.5343	0.036	33.3	1.5218	0.041
	100 γ	1	1	2	9	62.0	1.7926	0.031	38.4	1.5843	0.036

Table V - δ -HMX

	Sample Composition (wt Percent)	Prep Meth	Approx size of largest Delta HMX crystals (μ)	Test sample			Standard HMX (99.5% β -HMX)		
				h(cm)	m(log)	σ (log)	h(cm)	m(log)	σ (log)
T Y P E 12	70 δ , 30 β	10	70	15.0	1.1756	0.038	27.7	1.4426	0.031
	100- δ , trace β	9	1000	16.3	1.2134	0.034	25.4	1.4051	0.049
	97 δ , 3 β	9	1000	17.5	1.2438	0.150	25.9	1.4135	0.017
	100- δ , trace β	7	4	17.8	1.2509	0.063	26.7	1.4259	0.036
	60 δ , 40 β	10	> 40	18.5	1.2676	0.072	27.7	1.4426	0.031
	75 δ , 25 β	10	70	18.9	1.2760	0.076	27.7	1.4426	0.031
	100 δ	11	10	19.2	1.2843	0.049	21.6	1.3343	0.036
	67 δ , 33 β	10	80	19.8	1.2968	0.016	24.0	1.3801	0.043
	80 δ , 20 β	10	60	20.0	1.3010	0.089	27.7	1.4426	0.031
	90 δ , 10 β	10	100	22.4	1.3510	0.036	27.7	1.4426	0.031
T Y P E 12B	70 δ , 30 β	10	70	10.8	1.0347	0.112	29.4	1.4676	0.045
	80 δ , 20 β	10	60	11.5	incomplete test		29.4	1.4676	0.045
	75 δ , 25 β	10	70	11.6	1.0651	0.260	29.4	1.4676	0.045
	100- δ , trace β & α	12	4	11.8	1.0718	0.041	33.3	1.5218	0.054
	100- δ , trace β	9	1000	12.0	1.0801	0.026	31.7	1.5009	0.049
	90 δ , 10 β	10	100	12.2	1.0851	0.171	29.4	1.4676	0.045
	60 δ , 40 β	10	> 40	12.9	1.1119	0.196	29.4	1.4676	0.045
	97 δ , 3 β	9	1000	14.8	1.1710	0.146	28.1	1.4483	0.065
	100 δ	11	10	18.3	1.2619	0.051	26.1	1.4165	0.048

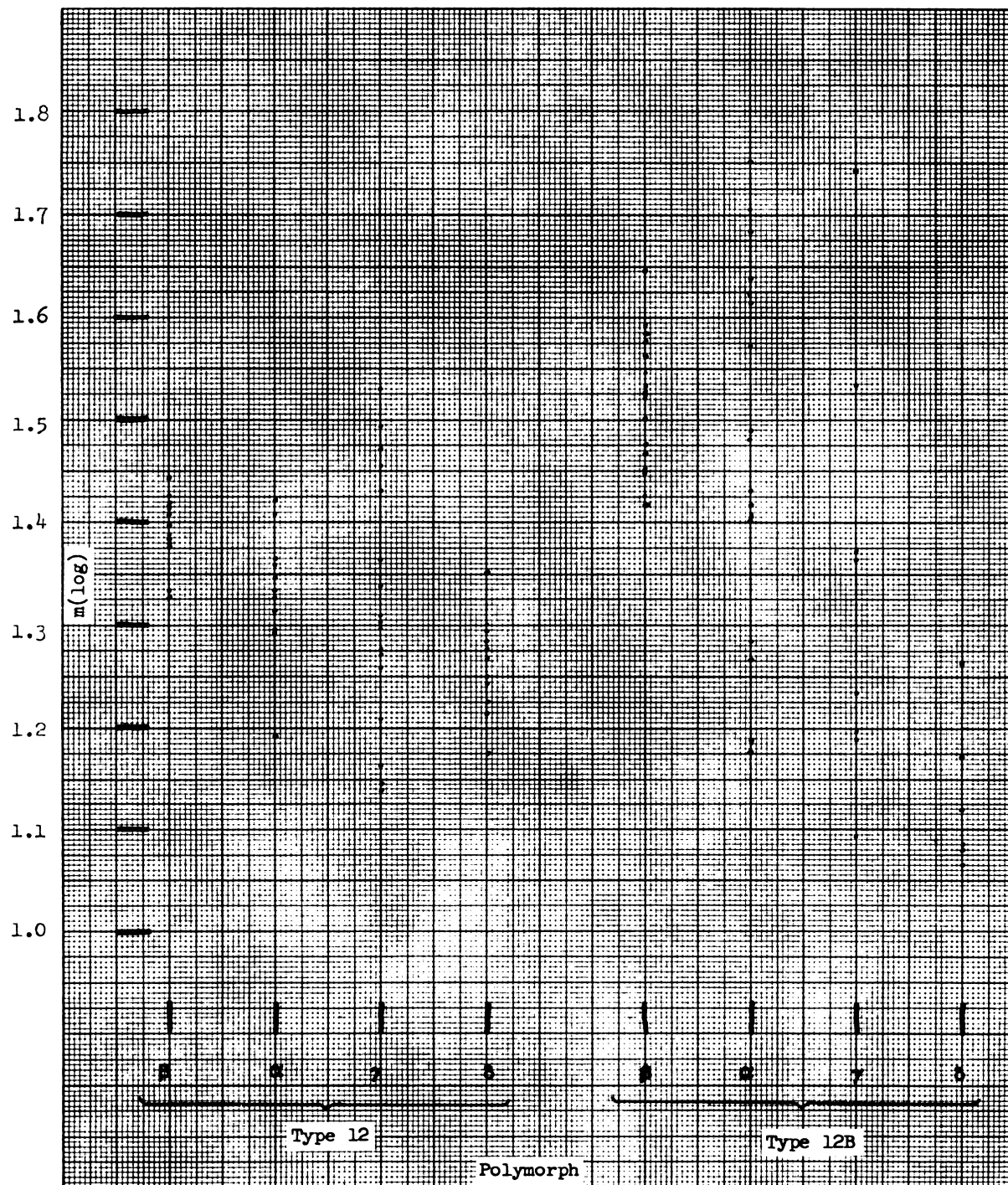


Figure 1

in most cases, contaminated with significant amounts of β -HMX, and Jeffers¹⁸ has reported that samples of δ -HMX containing crystals in the process of undergoing polymorphic transformation are more sensitive than samples of the pure polymorph. To the extent that the sample of pure δ -HMX was one of the least sensitive samples tested, our results tend to confirm that finding. Otherwise the sensitivities of the various δ -HMX samples do not correlate with their polymorphic composition. In any case, every sample of δ -HMX we have tested proved to be more sensitive - in some cases by a considerable margin - than the control sample of HMX which was run at the same time.

We also have the somewhat unusual result that δ -HMX is more sensitive when tested without the added grit provided by the sandpaper (ie, in the Type 12B machine).

Our work is in agreement with previous findings^{1,17} that the sensitivity of δ -HMX is independent of the crystal size and the method by which the sample is prepared.

The sensitivity data given in Table III for α -HMX cannot be correlated with crystal thickness, thickness of unstriated crystals, method of preparation, crystal imperfections, or contamination with solvent or other polymorphs. The various samples represent a considerable range of sensitivities, particularly in the case of the Type 12B machine. The Type 12 data for the most part suggest that α -HMX is only slightly more sensitive than β -HMX, though the sensitivity

of one sample approaches that of PETN. Several quite low 50% points appear in the collection of Type 12B data; these results otherwise can be summarized (rather imprecisely) by stating that, in this machine, α - and β -HMX appear to be in the same sensitivity class.

To put it another way, we find that most samples of α -HMX are not unduly sensitive; however, exceptions to this statement are not rare.

The sensitivity of α -HMX has been reported to increase with increasing thickness of the crystals^{11,18}. We are unable to confirm that conclusion. Jeffers¹⁸ noted exceptions to the trend and came to the conclusion that the sensitivity of α -HMX was controlled by some other factor, such as partial polymorphic transformation. In this connection it should be noted that Jeffers assumed that β -HMX is the stable polymorph at 130°C, rather than α .

Most of our observations about the sensitivity of α -HMX apply equally well to γ -HMX; however, there does appear to be a correlation between impact sensitivity and crystal size in the case of γ -HMX, with the larger (thicker) crystals being more sensitive. Similar results have been reported previously^{11,7}. Fine crystals of γ -HMX are about as sensitive as β -HMX, but crystals of a more usual size tend to lie between α - and δ -HMX in sensitivity.

We may summarize these results as follows.

- a) The impact sensitivity of β -HMX is reproducible and independent

of particle size. β -HMX is more sensitive than RDX in the Type 12B machine (without added grit) but is slightly less sensitive than RDX when tested with sandpaper in the Type 12 machine.

b) Although most of the samples of δ -HMX we have tested were contaminated with varying amounts of β -HMX, reasonably reproducible 50% points were obtained on this material. It is significantly more sensitive than β -HMX in both the Type 12 and Type 12B impact machines.

c) A wide range of 50% points is obtained with various preparations of α - and γ -HMX. While many of the samples resemble β -HMX in sensitivity, the more sensitive ones are in a class with δ -HMX. In the case of γ -HMX, sensitivity correlates with crystal size, the larger crystals being the more sensitive.

d) For crystals of a size likely to be encountered in practice, the order of sensitiveness of the HMX polymorphs is $\delta > \gamma > \alpha > \beta$.

2. The Impact Sensitivity of HMX as a Function of Temperature

The impact sensitivity of HMX was studied as a function of temperature, using electrically heated tools for this purpose. Useful results were obtained only with the Type 12 machine. The data are given in Table VI.

Our results are in qualitative agreement with those reported by Jeffers¹⁸, though the changes in sensitivity we observe are much smaller than those reported by him. The 50% point of β -HMX gradually decreases until a temperature of 150°C is reached; beyond that, the 50% points remain constant or, possibly, increase slightly.

Table VI - Heated HMX

Impact Temp (°C)	Time at Temp	Source of sample	Sample weight (mg)	Impact Sensitivity		
				h(cm)	m(log)	σ(log)
Room temp	Indefinite	Imp std HMX	40	27	1.432	
58	1 minute	"	"	20.0	1.3010	0.103
77	"	"	"	22.2	1.3468	0.061
98	"	"	"	18.7	1.2710	0.059
123	"	"	"	16.6	1.2210	0.073
150	"	"	"	14.7	1.1665	0.048
178	"	"	"	14.2	1.1510	0.036
200	"	"	"	16.8	1.2256	0.068
213	"	"	"	15.3	1.1843	0.036
Room Temp	Indefinite	99.5%	40	25.7	1.411	
128	1 minute	β-HMX	"	17.3	1.2385	0.026
150	"	"	"	14.6	1.1635	0.016
174	"	"	"	13.6	1.1343	0.023
202	"	"	"	15.0	1.1760	0.036
204	"	"	28	9.6	0.9843	0.036
128	21-23 hr	"	40	15.0	1.1760	0.036
150	"	"	"	14.4	1.1593	0.076
175	"	"	35	11.9	1.0756	0.053
200	"	"	28	14.3	1.1551	0.036

The results of the experiments on the effect of prolonged heating are confused by the partial decomposition and loss of weight of the sample which occurs. However, only at 200° does there appear to be a difference between the 1 min and 22 hr samples. The results obtained on the 28 mg samples indicate that the 1 min sample is the more sensitive. This again is in accord with Jeffers conclusion that partially transformed crystals are the most sensitive.

D. Crystallography of γ -HMX

The optical crystallography of γ -HMX has been studied by Blomquist¹ and McCrone⁴. Habits were not obtained which could be used to calculate axial ratios. The system was reported to be monoclinic with a beta angle of 120°. Later, both Small (as reported by Batty and Gilbert¹¹) and Krc¹⁴ studied this polymorph using X-ray diffraction. Their results are presented below together with data obtained by us by X-ray diffraction from a single crystal of γ -HMX.

X-Ray Diffraction of γ -HMX

Unit Cell		Krc	Small	This work
a		16.80	13.15	13.28
b		7.95	7.93	7.93
c		10.97	10.93	10.94
β		130°	105.5°	106.5°
Formula weights per cell		4	4	4
Density		1.79	1.79	1.78

Our results agree with those of Small, and there is no choice of axes which would give agreement with Krc. Systematic extinctions indicate an n glide perpendicular to b when conventional assignment of axes is used.

An alternate assignment for the unit cell is $a = 10.95$, $b = 7.93$, $c = 14.61$, and $\beta = 119.4^\circ$. This unit cell agrees with the morphology as described by McCrone. A single crystal has been examined which shows the zones 001, 100, 110, and 101 using McCrone's assignments. The optical properties of this are in agreement with those given by McCrone, and measurements of the interfacial angles give axial ratios in agreement with the alternate assignment for the X-ray unit cell. Systematic extinctions for this alternate unit cell indicate a space group of Pc or P2/c, with 4 molecules per unit cell.

Measurement of interfacial angles on twins of γ -HMX usually indicates a beta angle of 120° ; however, other angles are measured on occasion and indicate about 130° for the beta angle. These crystals have not been examined by X-ray diffraction to see if they differ from the one described earlier.

V. POLYMORPHIC TRANSFORMATIONS

Pure samples of the unstable polymorphs rarely transform into β -HMX at room temperature except in the presence of solvent or solvent vapor. The various conditions under which we have observed polymorphic transformations are described in the following paragraphs.

A. Solid Phase Transformations

1. $\beta - \delta$

The most common of the observed solid-solid transitions is that of β to δ at temperatures over 159°C . RDX has an effect on this transition,

especially in the temperature range from 159° to 175°C. Bachman HMX, 99.5% β -HMX, and β -HMX recrystallized from a solution saturated with RDX all transform easily to δ -HMX when heated at temperatures of 160° to 170°C, while the United Kingdom β -HMX, and β -HMX freed of RDX by recrystallization do not transform under identical conditions.

We first noticed the effect of RDX on the $\beta \rightarrow \delta$ transition when we were unsuccessful in an attempt to prepare single crystals of δ -HMX as pseudomorphs of fine recrystallized β -HMX by a heat treatment which we had used previously to prepare large single crystals of δ -HMX from 99.5% β -HMX. It was first thought that mechanical strains in the 99.5% material might be responsible for this difference in behavior, but mechanically strained recrystallized β -HMX also did not transform. RDX was isolated as the cause of the difference by the following experiment. First, 99.5% β -HMX was converted to γ -HMX by mixing an acetone solution of HMX with water. The γ -HMX was filtered, dried, and divided into two portions. One portion was added to a stirred suspension of Wabash RDX in a dilute acetone-water solution, while the other portion was added to a similar acetone-water solution which was free of RDX. Stirring was continued until all of the γ -HMX had converted to β -HMX. The crystalline products were filtered, dried, and centrifuged in zinc chloride solutions having a specific gravity of 1.860. Crystals with $\rho > 1.860$ were washed with water, dried, and percolated with hot 1,2-dichloroethane. The 1,2-dichloroethane removed the few entrained RDX crystals from the portion which had been transformed in the RDX suspension. The two

portions of β -HMX were heated at 163°C . The HMX recrystallized from a solution saturated with RDX converted to δ -HMX while the other portion showed no transformation. The HMX transformed in the presence of RDX was found by analysis to contain about 0.1 % RDX even though no crystalline RDX could be detected.

HMX containing RDX appears to form slip plane imperfections more easily under stress than pure HMX. This effect may be observed in $\eta = 1.59$ immersion oil between partly crossed polars, and could be related to the lower temperature required for the $\beta \rightarrow \delta$ transformation in HMX containing RDX.

The rate and mechanism of the $\beta \rightarrow \delta$ transformation when 99.5% β -HMX is heated has been studied, but not in detail. Preliminary results indicate that both the rate of nucleation and the rate at which the transformation zone spreads are greater in the presence of RDX. The effect of the RDX is most apparent at temperatures below 170°C .

The size of the δ -HMX crystals formed when 99.5% β -HMX is heated varies with the temperature. At temperatures below 163°C , the transformation zone moves slowly enough for the strains to be relieved, and a single crystal of β -HMX transforms into a single crystal of δ -HMX. The higher the temperature above 163°C , the smaller the δ -HMX crystals formed. This is caused more by a break-up of the transformation front than by multiple nucleation. Since RDX-free β -HMX will not transform into δ below 170°C , it is not possible to obtain large

crystals of δ -HMX from pure β -HMX.

δ -HMX crystals obtained by heating β -HMX are strained internally as is indicated by their behavior between crossed polars in the microscope. Also, the crystallographic axes of the δ crystal are randomly oriented with respect to those of the original β -HMX crystal.

If δ - and β -HMX are in intimate contact, the δ -HMX will convert to β -HMX by solid-solid transformation at room temperature. The velocity of the conversion is slow (about 0.02 mm/hr) and is always accompanied by decrepitation. Nucleation with β -HMX is essential for this transformation, and a preparation of δ -HMX free of β -HMX can be stored indefinitely without the transformation occurring. Grinding a mixture of δ - and β -HMX is a very effective way to nucleate the δ with β -HMX, and the transformation to β will take place rapidly after such grinding.

2. $\beta - \alpha$

If β -HMX, especially β -HMX free of RDX, is heated between 170°C and 190°C, α -HMX is produced in varying amounts. X-ray diffraction is by far the best method of detecting this α -HMX. Below 170°C no α -HMX is formed, and above 190°C the α formed transforms into δ -HMX. In general, the less RDX in the HMX, the more α -HMX formed. This is a result of the accelerating effect of RDX on the $\beta \rightarrow \delta$ transformation.

α -HMX has not been observed to transform into β -HMX by solid-solid transformation.

3. $\beta - \gamma$

The $\beta \rightarrow \gamma$ transformation has never been observed. The $\gamma \rightarrow \beta$ transformation does occur in the solid phase, but not as easily as the $\delta \rightarrow \beta$ transformation. Unstrained γ -HMX usually does not transform into β -HMX; however, strained γ -HMX does transform slowly to β -HMX at room temperature. X-irradiation of strained γ -HMX accelerates the transformation. An easy way to strain γ -HMX is by grinding, and grinding a mixture of γ - and β -HMX brings about rapid transformation.

4. $\alpha - \delta$

α -HMX will transform to δ -HMX at temperatures above 190°C. The transformation is nucleation controlled at these temperatures, since the velocity of the transformation front is very fast. Single crystals of the rod habit of α -HMX transform into single δ -HMX crystals.

The $\delta \rightarrow \alpha$ solid-solid transformation has not been observed.

5. $\gamma - \delta$

On the microscope hot stage γ -HMX has been observed to transform into δ -HMX at temperatures above 230°C by a very rapid solid-solid transformation. Each crystal of γ -HMX appears to transform to a single crystal of δ -HMX. However, a sample of γ -HMX containing a small amount of δ -HMX showed no evidence of a $\gamma - \delta$ transformation at a heating rate of 11°C/min in the differential thermal analysis apparatus¹⁵.

6. $\alpha - \gamma$

Transformations between these polymorphs have not been observed in the solid phase.

B. Transformations in the Presence of Solvents

There are at least three factors which have an influence on the behavior of the HMX polymorphs in contact with solvents. First, the phase rule implies that, at constant pressure and an arbitrarily chosen temperature, only one polymorph can be stable, and all of the other polymorphs will tend to transform to the stable polymorph. Second, there must be seed crystals of the various polymorphs present before the phase rule can be operative. If no mechanism for the formation of seed crystals of the stable polymorph exists, then an apparent anomalous stability will be observed.

The remaining factor is the solvent itself. The most important effects here are the solubility of HMX, the complexing and mobility of HMX in solution, and adsorption of solvent on the crystal surfaces.

Effects of all of these factors have been observed in studies of the behavior of the HMX polymorphs in contact with solvents. The thermodynamic stability ranges have been discussed earlier.

Seed crystal effects are common. For example, it would not have been possible to determine the $\beta - \delta$ transition temperature in the presence of solvents if seed crystals of α -HMX were present. Another

example of seed crystal effects occurs in the recrystallization of HMX from cyclohexanone when the cyclohexanone is removed from the solution by distillation. Rapid distillation of cyclohexanone from the conjugate system with water produces pure γ -HMX, while vacuum distillation of anhydrous cyclohexanone at the same rate and temperature produces δ -HMX. The implication is that seed crystals of γ -HMX are produced in the azeotropic distillation but not in the anhydrous distillation. Solution in water of small droplets of HMX-saturated cyclohexanone results in the formation of one γ -HMX crystal from each droplet.

Seed crystals of α -HMX form readily at the interface between solvent and the container, at least when the solvent wets the container. Myers and Bedard³ state that α -HMX is always formed when solvents are evaporated from HMX solutions. We have confirmed this observation in the case of nitric acid, acetic acid, CEF, and acetone. It was found that the initial point of appearance of α -HMX was always at the solvent-container junction. In the recrystallization of HMX from nitric acid it was possible to prevent the formation of α -HMX by preventing the evaporation of the solvent from the solvent-flask interface.

A good example of the effect of solvent is illustrated by the behavior, at room temperature, of a mixture of α -, β -, and γ -HMX in acetic acid or in a dilute acetone-water mixture with about the same solubility for HMX. In acetic acid the γ -HMX dissolves at a reasonable rate, and concurrently both the α - and β -HMX grow, with β -HMX growing by far the faster. As soon as the γ -HMX is consumed, all apparent

activity ceases. Mixtures of α - and β -HMX have existed together in contact with acetic acid for as long as a year. When acetone-water is the solvent the behavior of the system is the same until the γ -HMX is gone, at which time the α -HMX converts into β -HMX. Apparently there is a mechanism by which acetic acid slows the interchange between HMX in solution and the surface layer of HMX in a crystal of α -HMX.

It is possible that the rate of growth of the polymorphs is influenced by their crystallographic properties. Factors such as packing of the molecules and intermolecular forces at the surface of the crystal should influence the rate of growth; however, these factors could not be separated from possible solvent effects.

Rate of growth effects are useful in obtaining a variety of polymorphs under nearly the same conditions. If a solution of HMX in hot 70% nitric acid is seeded with a mixture of α -, β -, and γ -HMX it is possible to prepare, in a nearly pure state, any one of these polymorphs by controlling the rate of crystallization. Rapid cooling with stirring gives the γ polymorph. Slower cooling without stirring is selective for the α polymorph. Since β -HMX is thermodynamically stable, its formation is ensured by slow cooling and stirring. The formation of δ -HMX at 80°C in the presence of β -HMX during the rapid vacuum distillation of a solution of HMX in cyclohexanone is another example where rate of growth effects are controlling. Rate of growth effects are an alternate explanation to micro crystallites for

Blomquist's¹ observations on the effect of cooling rate on the polymorphic composition of recrystallized HMX¹.

A mixture of the polymorphs of HMX will convert to the β polymorph in the presence of solvent vapor. Except for the $\delta \rightarrow \beta$ transformation, there is every indication that the transformations occur through a solvent phase. Corners of the unstable crystals become rounded, and only well-formed single β -HMX crystals with a recognizable habit are formed from α - or γ -HMX.

C. Behavior of HMX in Partially Miscible Solvent/Water Systems

Myers and Bedard³ were the first to report that γ -HMX is formed when a cyclohexanone solution of HMX is steam distilled. This observation is of special interest since systems of this general sort may be involved in the manufacture of HMX and in the preparation of plastic bonded explosives by the water-slurry method. A number of experiments were, therefore, carried out at LASL for the purpose of verifying and extending the Canadian results. We note here that the reflux temperature of the two-phase cyclohexanone/water system is 88°C at Los Alamos, or 8°C below its boiling temperature at the CARDE laboratory.

We first studied the effect of varying the rate at which the cyclohexanone was removed from the system in order to determine whether the polymorph produced was influenced by this rate. In this set of experiments a flask containing initially 45 cc of water and 10 cc of

cyclohexanone saturated with HMX was fitted with a variable reflux ratio head. This flask was then placed in an oil bath thermostated at 130°C to a depth such that the water level in the flask, when all the cyclohexanone had been removed, was higher than the oil level. Even at the fastest distillation rate, about six minutes elapsed before any crystals of HMX appeared. The results of these experiments are summarized below.

Reflux Ratio	Distillation Time for 2 Phases plus γ -HMX	Est Yield of Polymorphs (wt Percent) (Microscopic Examination)		
		<u>Gamma</u>	<u>Alpha</u>	<u>Beta</u>
0.00	6 min	100	trace	0
0.875	48 min	97	< 2	< 1
0.933	90 min	90	10	0
0.95	120 min	95	5	0
0.97	200 min	< 1-	0	> 99
0.975	240 min	1-3	> 0	98

In the estimated yield table, > 0 means just detectable, trace means evidence for seed crystals (in that α -HMX was observed to form on addition of a solvent), and 0 means not detected at all. The estimated yield is based on mass and not on numbers of crystals. In the 240-min case, for example, the estimated numbers of crystals are about 60 β to 40 γ .

The second series of experiments was similar to the first except that the distillation was run at its fastest rate until one minute after the presence of γ -HMX crystals was detected. The distillation was then stopped, and the pot containing cyclohexanone, water, and γ -HMX was allowed to reflux for various lengths of time. After

this period of time the distillation was restarted and the cyclohexanone was removed as rapidly as possible. It took about six minutes to distill off the cyclohexanone layer. The results of these experiments are summarized below.

<u>Reflux Time</u> <u>(Min)</u>	<u>Est. Yield of Polymorphs (wt. percent)</u>		
	<u>Gamma</u>	<u>Alpha</u>	<u>Beta</u>
0	100	trace	0
57	70	30	0
60	75	25	0
120	60	40	0
132	9	1	90
170	35	60	5
242	> 0	0	< 100
40*	10	0	90

*In this experiment the pot was seeded with beta HMX after the gamma HMX appeared and just before the reflux time started.

Both of these experiments indicate a fairly long induction time for the formation of seed crystals of β -HMX.

In the third type of experiment conditions were varied so that there was always a large surplus of β -HMX present. The pot contained 1 gm of β -HMX, 45 cc of water, and 10 cc of cyclohexanone initially. In one experiment the pot was refluxed for 20 hours and the cyclohexanone was then removed in 14 minutes. γ -HMX was barely detectable in the HMX from this experiment. In another experiment the cyclohexanone was removed without allowing a reflux time for the cyclohexanone to become saturated with HMX. No γ -HMX was detected in the HMX from this experiment. In the same type of experiment γ -HMX was always detected

when steam was used as the heat source.

The effect of temperature of distillation on the polymorph of HMX formed in the steam distillation of cyclohexanone was determined by lowering the pressure in the system to 5 cm. This reduced the reflux temperature to 37°C. The temperature of the heating bath was lowered so as to obtain about the same distillation rate. γ -HMX was still the principal product of this distillation provided no seed crystals of β -HMX were present at the time the system became supersaturated with HMX.

One of the major changes which occurs in the cyclohexanone/water system on lowering the temperature is a considerable decrease in the solubility of cyclohexanone in the water-rich phase. An extension of this effect to the point that water was eliminated from the system seemed an interesting experiment. It was decided to distill the dry cyclohexanone under a pressure of 5 cm (bp 72°C) in order to reduce the temperature of the distillation to the previously studied temperature range. The distillation flask was heated by a hot-water bath so that the temperature could nowhere exceed that of the water. In the first experiment, 15 cc of cyclohexanone saturated with HMX at room temperature was distilled to dryness. The distillation required about six minutes. The crystalline HMX remaining in the distillation flask was examined and was found to be almost 100% the δ polymorph in the presence of a trace of β . The presence of δ was surprising, especially with β present, because the rate of the $\delta \rightarrow \beta$ transformation in HMX-saturated cyclohexanone at 72°C should be less than the distillation time.

Another experiment, the same as the previous one except for the amount of HMX, was performed. The amount of HMX was increased sufficiently to ensure a slight excess of crystalline β -HMX at all times during the distillation. Examination of the crystalline HMX from this experiment showed that most of the HMX which had been in solution came out in the δ form. This experiment indicates that the rate of growth of δ -HMX must be much faster than that of β -HMX under the conditions of supersaturation which existed in this experiment. In order to check this hypothesis, a further experiment, the same except for halving the distillation rate (water bath 80°C), was performed. This decrease in the degree of supersaturation or increase in time was sufficient to allow the crystallized HMX to occur almost entirely in the form of the β polymorph, an expected result.

The source of the γ -HMX seed crystals in the cyclohexanone/water system may be related to the solution of the cyclohexanone-rich phase in the water-rich phase as the steam distillation progresses. When small droplets of cyclohexanone saturated with HMX are introduced into the bottom of a column of water tall enough so that the cyclohexanone dissolves in the water before the droplet reaches the top surface, then crystals of γ -HMX are produced (X-ray identification).

The most important conclusion concerning the behavior of HMX in the cyclohexanone/water system is that it is very difficult to avoid the formation of traces of γ -HMX during the distillation to remove the cyclohexanone. γ -HMX is most likely to occur as a deposit on the parts

of the equipment which are hotter than the boiling point of the two phase system. The orifice of a steam jet would be a likely point to locate γ -HMX even though none could be detected in the major portion of the recrystallized HMX. In addition, α -HMX was a common product. While α -HMX is not likely to be a problem in the recrystallization of HMX from cyclohexanone, the formation of traces of α might cause trouble because of the slow $\alpha \rightarrow \beta$ transformation in the presence of water.

A few experiments with other solvents for HMX in the presence of water indicate that the formation of γ -HMX in the cyclohexanone/water system is not unique. At room temperature a solution of HMX in 2-butanone was added, with rapid stirring, to enough water to dissolve the 2-butanone. The HMX which precipitated was identified (X-ray) as γ -HMX.

Steam distillation of 2-butanone, n-butyl acetate, or toluene saturated with HMX left a residue which contained appreciable amounts of γ -HMX.

Partially miscible systems are not required for the formation of γ -HMX by precipitation as one of the easiest methods for the preparation of γ -HMX is by the addition of an acetone solution to an excess of water.

APPENDIX

Analytical and Test Procedures

I. IDENTIFICATION AND ANALYSIS OF THE POLYMORPHS

Three methods of analysis were used in this investigation - visual with the aid of a polarizing microscope, infrared using the KBr pellet technique, and X-ray diffraction. Optical properties described by Blomquist¹ and McCrone⁴ were the basis of the most rapid qualitative and rough quantitative analysis. Estimates of crystal size were obtained at the same time using an eye piece micrometer.

The infrared spectra of the HMX polymorphs differ, and in principle this property should be satisfactory for analysis. Myers and Bedard³ and Picard et al.⁵ studied the problem in a preliminary manner using mujol mulls. This method of analysis was investigated using the KBr pellet technique instead of a mull. The method was satisfactory for the pure polymorphs, but not for quantitative analysis of polymorphic mixtures because of the ready conversion of the γ and δ polymorphs to the β polymorph during and after the grinding operation whenever any β -HMX was present initially.

Infrared spectra of the polymorphs are shown in Figures 1A and 2A. The curves are a composite of the KBr and NaCl spectral regions. They are similar to the spectra given in refs. 3 and 5 except for the

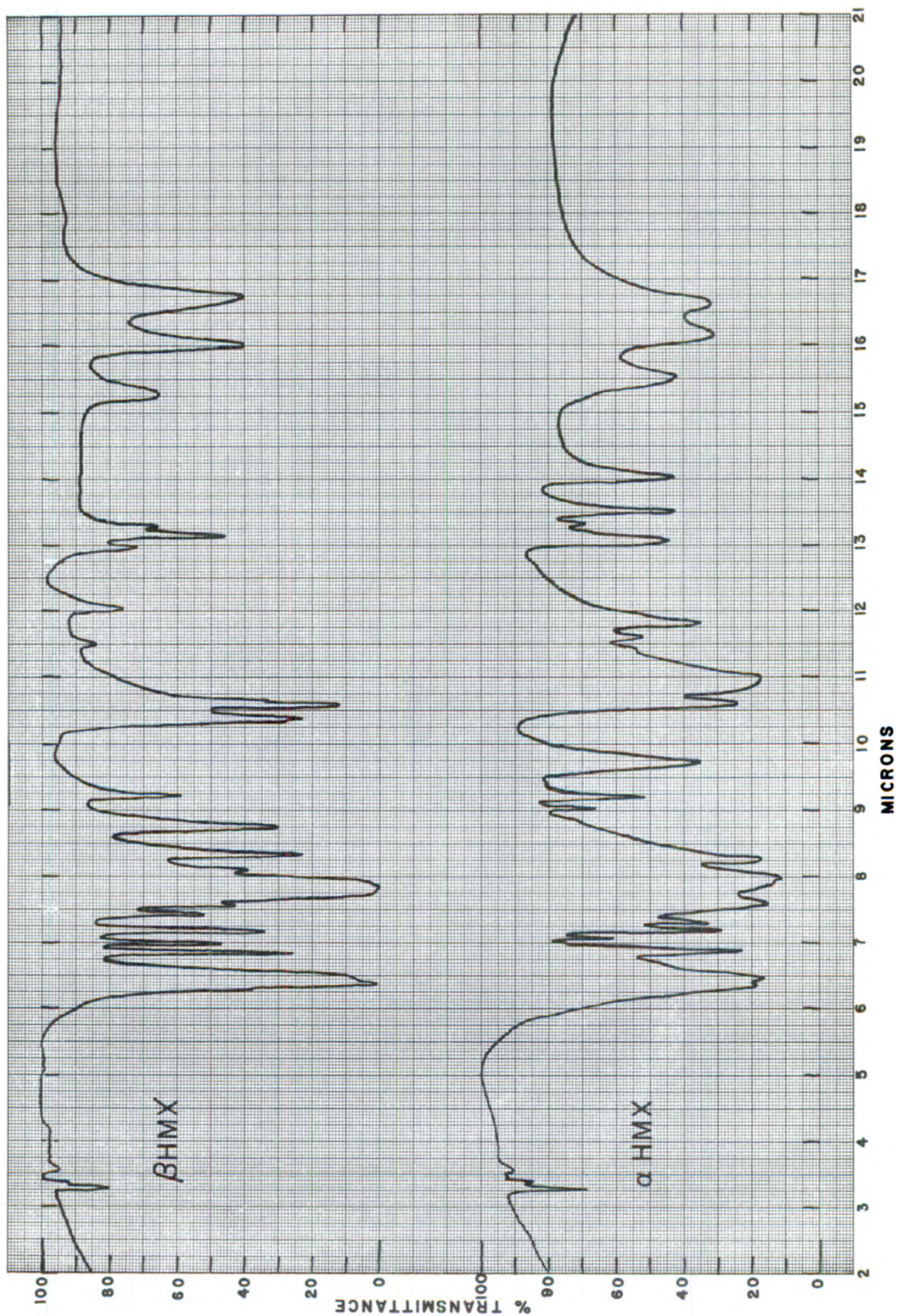


Figure 1A

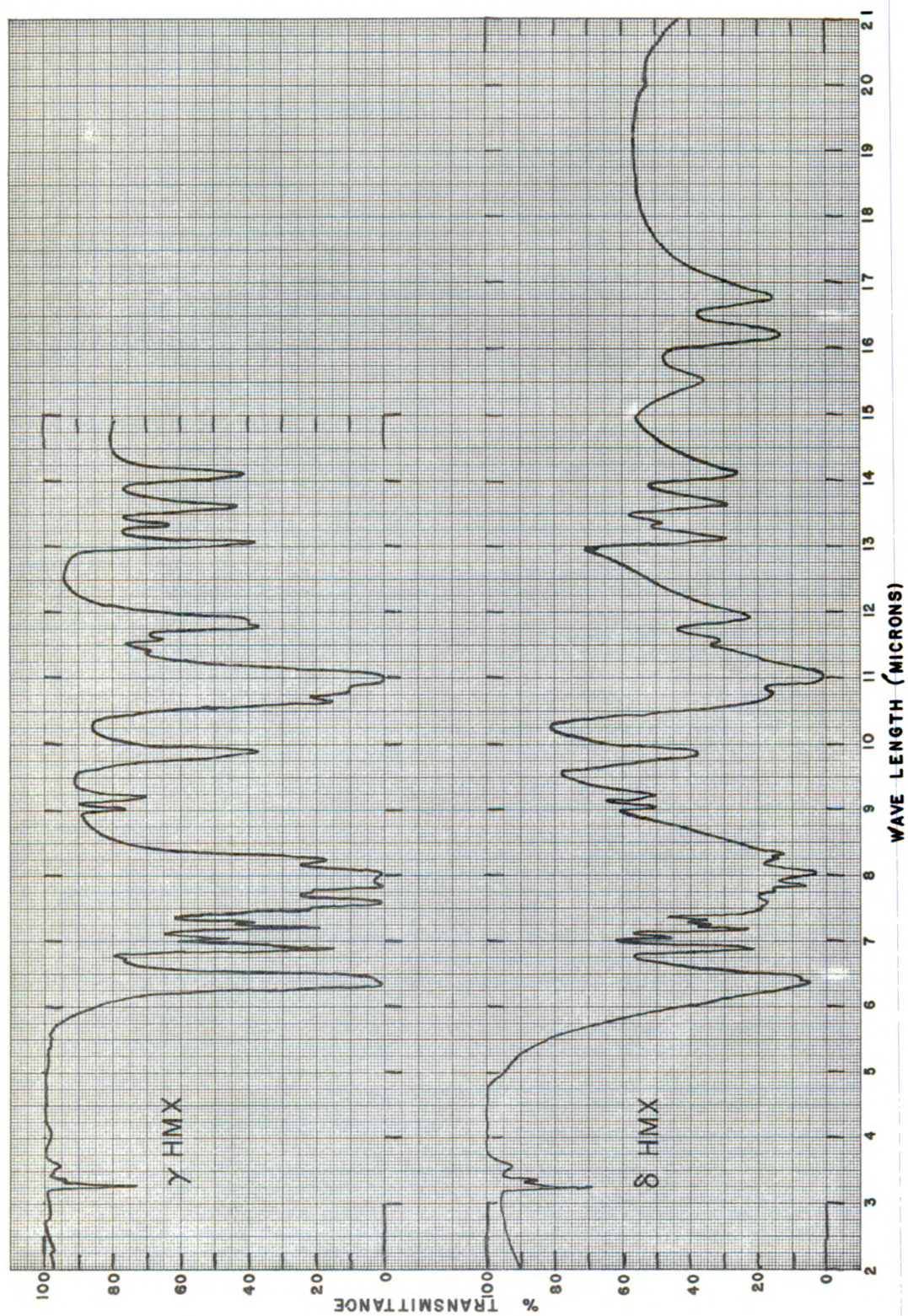


Figure 2A

increased range and resolution. The spectrum of the δ polymorph contains weak bands at 21.22 and 23.80 μ in addition to those shown. Infrared analysis was not studied in detail since nearly pure samples of the polymorphs are more easily analyzed microscopically.

X-ray diffraction is a classical method for distinguishing polymorphs. This method was not entirely satisfactory in the case of the HMX polymorphs. The necessity for grinding the samples, in many cases, was one of the principal sources of difficulty. As has been mentioned in the body of this report, γ - and δ -HMX tend to convert to β -HMX when ground in the presence of β -HMX. The conversion of γ -HMX to β -HMX by solid-solid transition also is accelerated by X-irradiation if the γ -HMX has been strained by grinding. Visible and infrared light do not have the same accelerating effect. Fine crystals of α -HMX strain very easily, and this strain affects the X-ray diffraction pattern. It is very difficult to eliminate orientation effects in the cases of the α and γ polymorphs due to their habits. For these reasons X-ray diffraction was only useful as a qualitative analysis tool.

The X-ray diffraction patterns for the various polymorphs are given in Table 1A. The β -HMX sample consisted of essentially spherical crystals 21 μ in diameter. The α -HMX sample was prepared by grinding a preparation which contained only very thick crystals - a procedure which did not induce detectable strain. The resulting crystals are still short rods and it is likely that the diffraction intensities are

Table 1A

X-ray Diffraction Data for the HMX Polymorphs

β -HMX		α -HMX		γ -HMX		δ -HMX	
"d", Å	I/I ₁	"d", Å	I/I ₁	"d", Å	I/I ₁	"d", Å	I/I ₁
6.03	40	6.38	3	9.50	13	6.65	96
5.50	36	5.97	77	7.87	7	6.50	27
5.37	1	5.37	9	7.11	8	6.15	13
4.84	9	4.52	4	6.70	6	5.66	61
4.31	100	3.78	18	6.33	100	5.40	87
4.01	9	3.61	15	6.08	58	5.14	82
3.848	42	3.52	100	5.24	79	4.64	11
3.588	1	3.46	5	4.94	9	4.20	34
3.396	30	3.195	1	4.77	27	3.81	46
3.302	10	2.989	34	4.46	34	3.74	24
3.262	24	2.900	3	4.36	25	3.62	100
3.180	9	2.869	1	4.25	2	3.47	62
3.055	13	2.802	1	4.11	8	3.31	14
3.000	38	2.745	13	4.07	15	3.26	10
2.933	3	2.678	2	3.93	2	3.173	60
2.796	72	2.550	2	3.83	41	3.130	52
2.756	5	2.467	12	3.72	35	3.080	5
2.694	3	2.392	2	3.64	4	2.961	7
2.57	1	2.381	2	3.56	16	2.914	11
2.530	3	2.343	3	3.48	34	2.836	3
2.455	2	2.322	6	3.45	6	2.792	6
2.421	10	2.278	5	3.33	14	2.702	35
2.41	8	2.185	2	3.30	12	2.630	12
2.366	1	2.023	1	3.25	26	2.510	22
2.262	3	1.992	2	3.16	33	2.450	8
2.224	1	1.927	3	3.14	27	2.406	4
2.186	9	1.893	2	3.048	13	2.319	15
2.161	2	1.803	1	2.944	14	2.256	47
2.131	4	1.762	1	2.911	13	2.239	14
2.085	4	1.614	2	2.879	4	2.186	4
2.010	3			2.716	23	2.143	10
1.983	1			2.672	9	2.056	3
1.957	2			2.643	9	1.998	3
1.926	1			2.617	15	1.991	5
1.909	1			2.573	10	1.918	3
1.897	2			2.545	12	1.901	3
1.869	3			2.508	4	1.891	4
1.86	2			2.482	4	1.847	5
1.815	2			2.460	8	1.815	2

Table 1A (continued)

β -HMX		α -HMX		γ -HMX		δ -HMX	
"d", Å	I/I ₁	"d", Å	I/I ₁	"d", Å	I/I ₁	"d", Å	I/I ₁
1.795	5			2.418	7	1.798	2
1.77	1			2.315	4	1.779	1
1.709	1			2.273	5	1.751	2
1.668	2			2.237	6	1.708	3
1.655	1			2.219	4	1.686	1
1.548	2			2.19	2	1.657	2
1.528	1			2.164	3	1.644	2
1.520	1			2.109	6	1.634	1
1.463	1			2.096	5	1.608	1
1.338	1			2.062	4	1.594	1
				2.034	3	1.527	2
				2.023	5	1.505	2
				1.999	1	1.486	1
				1.918	1	1.451	1
				1.894	2	1.445	2
				1.877	2	1.441	1
				1.847	1		
				1.824	1		
				1.789	2		
				1.781	2		
				1.770	3		
				1.760	4		
				1.742	2		
				1.732	2		
				1.680	2		
				1.675	2		
				1.529	2		
				1.459	1		

affected by nonrandom orientation of the α -HMX crystals. The γ -HMX sample was prepared from crystals which were triangular plates about 20 μ wide by 4 μ thick and also may show orientation effects. The δ -HMX sample was prepared by heating 99.5% β -HMX so that only small (10 μ) randomly oriented crystals of δ -HMX were formed.

The samples were packed into the standard sample holders for the North American Philips X-ray Diffractometer in the manner described by Klug and Alexander⁶. The diffractometer had been aligned by the procedure described by Parrish and Lowitzsch⁷ and the measured 2θ values corrected for the various systematic errors described in the same article. The intensity data are based on the peak intensities recorded and are normalized to make the strongest line 100. Copper radiation was used. The definition of I/I_1 is $100 \times I/I_{100}$ and only lines with intensities such that I/I_1 is 1.0 or above are reported.

The powder pattern of β -HMX has been published by Soldate and Noyes⁸, Krc⁹, and Rosen, Taylor, and Wintermoyer¹⁰. Rosen, Taylor, and Wintermoyer also give the diffraction for α - and γ -HMX. However, they ground their samples and their sample of γ -HMX was almost completely transformed into β -HMX by the time the pattern was obtained. The γ -HMX remaining in their sample gives a pattern corresponding to extremely small, thin crystals.

II. ANALYSIS FOR RDX IN HMX

This was done by the procedure described by Yasuda and Rogers¹⁹.

The method involves the separation of the RDX from the HMX by paper chromatography using a formamide/ethylene chloride system. The RDX is then determined colorimetrically.

III. IMPACT SENSITIVITY MEASUREMENTS

The standard impact sensitivity test used at LASL is an improved version of the ERL Type 12 machine which has been described in numerous reports.²⁰ The improvements which have been made leave the basic test geometry unchanged. The sample (40 mg) is still placed on a small square of sandpaper and then impacted between hardened steel cylinders by a 2.5 kg weight.

A modification of this test, known as the Type 12B test, also is being used occasionally. The Type 12B machine differs from the Type 12 only in that the sandpaper is omitted and the flat surfaces of the steel and anvil are roughened by sandblasting with 40 grit carborundum. The two devices together are intended to probe the impact sensitivity of an explosive both with and without the added grit represented by the sandpaper. Unfortunately, the Type 12B test suffers from a lack of reproducibility which limits its usefulness and imposes severe restrictions on the reliability of the data.

The up-and-down test procedure²¹ is used with both machines with logarithmically spaced height intervals. The data given in the tables in this report are the 50% explosion height in cm (h), its logarithm to the base 10 (m), and the population standard deviation in log units

(σ). All the tests reported here were 25-shot tests. An approximate value for the standard error of \bar{m} can be obtained by multiplying σ by 0.29 (this factor varies slightly from run to run).

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